ORGANOMETALLIC ELECTROLYTE OF HIGH CONDUCTIVITY
FOR CATHODIC DEPOSITION OF SODIUM

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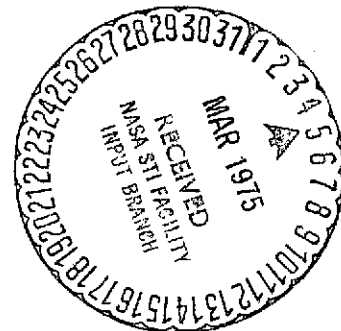
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16. Abstract

An organometallic electrolyte of high conductivity for the cathodic deposition of Na consists of a mixture of $NaAlMe_4$ (30-75 mole%) and $NaAlEt_4$ (70-25 mole%). The mixture may also contain small amounts of a corresponding alkoxy complex compound.

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ORGANOMETALLIC ELECTROLYTE OF HIGH CONDUCTIVITY
FOR CATHODIC DEPOSITION OF SODIUM

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are named as inventors.

ABSTRACT: An organometallic electrolyte of high
conductivity for the cathodic deposition of Na consists of
a mixture of $NaAlMe_4$ (30-75 mole%) and $NaAlEt_4$ (70-25
mole %). The mixture may also contain small amounts
of a corresponding alkoxy complex compound.

As is well known, metallic sodium can only be separated   / [1*]
from electrolytes which contain no water. Sodium can be obtain-
ed from aqueous solutions only in the form of sodium amalgam,
using a mercury cathode. The industrial processes for
production of metallic sodium work with fused anhydrous
hydroxide or with fused sodium chloride, the melting point
of which is decreased by addition of certain amounts of calcium
chloride. The operating temperatures of the corresponding
electrolytic cells are 330 and 630°C, respectively. The
properties of the electrolyte and the high operating temperatures
place significant requirements on the material used for

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* Translator's Note: numbers in margin indicate pagination
  of original foreign text.

1

construction of the cell. Neither electrolyte, furthermore, is suited for a process in which a sodium-containing material is used as the anode, from which the sodium is to be dissolved in the course of the electrolysis and deposited cathodically as sodium metal. A practically important sodium-containing material, currently used industrially in certain embodiments of alkali chloride electrolysis is sodium amalgam. The deposition of metallic sodium from sodium amalgam is a technically interesting problem which has often been worked on. Various suggestions have been made. In particular, there have been recommendations for electrolytes consisting of mixtures of sodium hydroxide, sodium iodide and sodium bromide. These mixtures melt at 217°C, and one can operate electrolytic cells with them at an operating temperature of 230 to 250°C. This temperature is about 100° C below the boiling point of the mercury, while molten sodium hydroxide alone is not useful in such a cell because one must work practically at the boiling point of the mercury, which would cause excessive problems.

Although the problem of obtaining sodium from sodium amalgam, considered economically, is very stimulating, none of the suggested methods have prevailed in large extent in practice. One reason for this is that the sodium contains several percent of mercury, which is difficult to eliminate. Such a necessary after-treatment decisively limits the economy of the whole process.

Along with such a winning of sodium from sodium amalgam, the electrolytic refining of crude sodium is also technologically important. Recently, for instance, large amounts of sodium of particularly high purity are being used as heat carriers.   /2

2

This sodium has so far been obtained essentially by distillation of metallic sodium in vacuo. But this is an operation which is not at all simple, and in which it it difficult to exclude the last traces of oxygen or sodium oxide, because penetration of air must always be expected to a certain extent in technological equipment under vacuum. Such difficulties were not expected for a technologically accessible electrolytic purification of sodium.

In Patent 1,114,330 it is recommended that sodium be deposited from melts of certain alkali aluminum organic complex compounds. The electrolyte principally considered for this purpose is fused sodium aluminum tetraethyl with the formula $NaAl(C_2H_5)_4$. This compound has a melting point of 125°C. With this, correspondingly, it is possible to operate at a temperature about 100°C below the temperature of the lowest-melting purely inorganic electrolytes. This gives so many advantages for the construction of the corresponding equipment that one can calmly accept the rather inconvenient property of sodium aluminum tetraethyl, that of igniting in the air. This is even more true because one must in any case operate in the absence of air with fused alkali metals, which in every case separate in such electrolytic cells.

The only property of sodium aluminum tetraethyl which is less favorable for electrolysis is a rather low conductivity. At the melting point it is $5 \cdot 10^{-2}$ $\Omega^{-1} cm^{-1}$. The conductivity can be improved, and the melting point reduced even more, by addition of potassium aluminum tetraethyl. Of course, one cannot convert to pure potassium aluminum tetraethyl, which has a conductivity of $12 \cdot 10^{-2}$ $\Omega^{-1} cm^{-1}$ at 125°C, because it is sodium which is to be deposited. The potassium aluminum tetraethyl is not even suitable for the deposition of potassium because it has not yet been possible to separate potassium at all well in electrolytes of this type. In the extreme case,

one can use mixtures with at least 20% sodium aluminum
tetraethyl. These electrolytes deposit practically only
sodium in the electrolysis by the method of the patent
mentioned, particularly with use of sodium-containing anodes.

In practical use, however, such electrolytes exhibit
the following problem:

Near the cathode the electrolyte becomes depleted of
sodium. Then separation of potassium also begins. This can
lead to disturbances in the entire electrolysis mechanism.

One must, therefore, take care to have extremely good
mixing of the electrolyte during the operation of the cell.
Nevertheless, problems can occur, especially at high current
densities and especially with use of the so-called net cathodes,
because the concentration equilibration within the electrolyte
is made difficult by the fibers of the net itself. The
individual fibers of the net in a net cathode are yarns of
much smaller fibrils with corresponding capillary interspaces
which draw in the electrolytes. The portions of the electro-
lyte bound here, which are exposed to direct electrolytic
decomposition, mix only difficultly with other portions of
the electrolytic bath. It appears, therefore, that this attempt
to increase the conductivity is also limited in its practical
effect.

But the net cathode is of exceeding practical importance
for the operation of such cells. As is well known, these cells
have a very fine cloth of cellulose or, in particular, glass
fibers, stretched at a very small distance from a cathode surface,
such as copper. This does not decisively reduce the conduct-
ivity of the electrolyte, but it cannot be penetrated by
metallic sodium because the opposing capillary forces are
too great. By means of this artifice, one can manipulate even

4

large cathode areas of liquid sodium just as conveniently as if they were of a solid material.

For all these reasons it is urgently desirable to develop an electrolyte which contains only sodium as the cation, with appropriately higher conductivity. The path to the discovery is in the knowledge that mixtures of certain sodium aluminum organic complex compounds contribute to the increase of the conductivity similarly to mixtures of sodium and potassium tetraethyl.

The subject of the invention is an organometallic electrolyte mixture of good conductivity, containing sodium aluminum complex compounds of the general formula $NaAlR_4$ (R = alkyl residue) for the cathodic deposition of sodium, characterized by containing a mixture of $NaAl(CH_3)_4$ and $NaAl(C_2H_5)_4$. In particular, according to the invention, this electrolyte mixture consists of 30 to 75 mole percent of the $NaAl(CH_3)_4$ complex compound and of 70 to 25 mole percent of the $NaAl(C_2H_5)_4$ complex compound. Preferably, there are at least equivalent amounts of the two compounds with respect to the $NaAl(CH_3)_4$.

The conductivity of an exactly equimolar mixture of the two complex compounds at 130°C is $10 \cdot 10^{-2}\ \Omega^{-1}\mathrm{cm}^{-1}$. This corresponds to that of an equimolar mixture of sodium and potassium aluminum tetraethyl. The advantage of the mixture according to the invention over this well-known mixture, however, is that only sodium-containing complex compounds are used here. Equally well, the increase of the conductivity by addition of sodium aluminum tetramethyl to sodium aluminum tetraethyl alone might not yet have sufficed to make such a mixed electrolyte practically important. But the mixtures according to the invention show still a second unexpected and technically extremely significant property.

Sodium aluminum tetramethyl melts very high, at 240°C. This melt would presumably have a highly favorable conductivity, but the sodium aluminum tetramethyl is not sufficiently stable at the melting temperature, and decomposes. Furthermore, very apparent theoretical considerations show that the mercury content of the sodium dissolved from amalgam anodes and deposited again must be higher, the higher the operating temperature of the electrolytic cell. Thus, with sodium aluminum tetramethyl one would gain nothing over the strictly inorganic salt mixtures previously recommended. Surprisingly, the two compounds, the tetraethyl and the tetramethyl complexes, exhibit an unusually low eutectic. The eutectic melt is completely liquid above 83°C, and is to this extent entirely equivalent to the mixed electrolyte of potassium and sodium aluminum tetraethyl compounds. The fusion diagram of the two materials [NaAl(C$_2$H$_5$)$_4$ is abbreviated as "NaAlEt$_4$"] is presented in the figure. Its conductivity has the value given above at 130°C, $10 \cdot 10^{-2}$ Ω^{-1}cm^{-1}. Furthermore, this increases along the right rising branch of the fusion diagram. It can be brought to some 13 to 15 $\cdot 10^{-2}$ Ω^{-1}cm^{-1} without any decisively bad effect on the melting characteristic.

The working voltage required is decisive for the energy consumption of an electrolysis cell. Electrolysis according to this invention makes it possible to avoid completely the technical problems at the sodium net cathodes resulting from the admixture of potassium. The invention also makes it possible to reduce the working voltage by factors between 0.3 or 0.4 on one hand and 0.75 on the other hand, in comparison to the best-known electrolytes of this type containing only sodium. Alternatively, it is possible to operate

cells with this voltage, utilizing some 1.35 to 3 times as much electrical energy as with a filling of sodium aluminum tetraethyl, giving 1.35 to 3 times the production with the same investment. The preferred range of electrolyte

composition according to the invention is indicated in the figure by the vertical dashed lines.

In practical operation, it is convenient to replace the electrolyte with slight amounts — a few percent — of the corresponding sodium alkoxyaluminum trialkyl compound, causing only an insignificant reduction in the conductivity. This protects the cathodically deposited sodium from the aluminum. This is most simply done by adding a small amount of an alcohol to the electrolyte mixture.

The production of sodium aluminum tetraethyl, one component of the electrolyte mixture according to the invention, is adequately described in the literature. The other component, sodium aluminum tetramethyl, can be prepared by one of the following processes, for instance:

Example 1

50 g (= 2.18 gram atom) sodium are heated in a dry one-liter three-neck flask, filled with inert gas and fitted with a stirrer, reflux condenser and dropping funnel, to 180°C. With stirring, one drops 100 cm^3 (= 96 g = 1.04 mole) $Al(CH_3)_2Cl$ onto the molten sodium. When all the dimethyl aluminum chloride is added, the powdery reaction mixture is allowed to cool with stirring. Then 300 cm^3 dry diethyl ether is added and the mixture is stirred for 20 minutes. After the stirring is stopped, one allows the solid products, NaCl and aluminum, to settle, siphons off the clear ether solution of $NaAl(CH_3)_4$, and extracts the residue three times with 200 cm^3 ether. The combined solutions, after distilling off the ether and drying in a vauum of 10^{-3} Torr, yield 55 g (= 0.5 mole) $NaAl(CH_3)_4$. The analytical data for the

substance are:

Found . . . . Na 20.95%; Al 24.6%; CH$_3$ 54.2%
Calculated . Na 20.9%; Al 24.6%; CH$_3$ 54.6%

The yield is 96.5%.

Example 2

In the same way as described in Example 1, NaAl(CH$_3$)$_4$ can be prepared by dropping 48.3 g (= 0.67 mole) Al(CH$_3$)$_3$ onto 11.5 (= 0.5 gram atom) molten sodium at 180 to 200°C. The yield and purity of the product are of similar quality to those described in Example 1.

Example 3

9.7 g (= 58.4 mmol) NaAl(C$_2$H$_5$)$_4$ are dissolved in 50 cm^3 benzene at 70°C with stirring. Into the solution, one drops a solution of 5.6 g (= 78 mmol) Al(CH$_3$)$_3$ in 20 cm^3 benzene. A white, insoluble precipitate forms immediately. The reaction mixture is allowed to stir for another hour, and then the precipitate is filtered, with the usual precautions for working with organometallic compounds which are sensitive to air and moisture. The precipitate is dried at 10^{-3} Torr and 150°C. The 6.2 g (= 56.3 mmol) NaAl(CH$_3$)$_4$ are analytically /6 pure. The yield is 96.5% of theory. NaAl(CH$_3$)$_4$ melts at 238°C without decomposition.

The mixtures of sodium aluminum tetramethyl and tetraethyl according to the invention can also be produced very simply by adding the necessary amount of sodium aluminum tetramethyl to molten sodium aluminum tetraethyl, with the air excluded,

or by dissolving both materials in dry, air-free diethyl
ether or tetrahydrofuran and evaporating this solution.
But one can also combine the production of the mixtures
directly with the production of the alkali aluminum tetraalkyl
compounds. Examples 4 to 8 describe this.

Example 4

One proceeds at first as described in Figure 3, but
does not filter off the precipitate of sodium aluminum tetra-
methyl. Rather, one adds   to the reaction mixture, which
still contains free aluminum triethyl, 1.9 g sodium
hydride, conveniently in the form of a 20% suspension in
mineral oil. The mixture is then stirred for one hour at
100°C. The mixture is then charged into an autoclave of
200 cm^3 capacity, with exclusion of air, and heated with
shaking at 160°C. The ethylene (20 at) is rapidly absorbed. When
the pressure remains constant, one can cool the autoclave
to 100°C, discharge the excess ethylene, and remove the
liquid contents from the autoclave, with exclusion of air.
Now there are two layers. The upper layer is practically solely
the mineral oil introduced with the sodium hydride. The
lower layer is a mixture of sodium aluminum tetraethyl and
sodium aluminum tetramethyl in the molar ratio of 4:3, as
described in the invention.

Example 5

One does as described in Example 1, allowing a mixture
of 48 g (= 0.5 mole) Al(CH$_3$)$_2$Cl and 60 g (= 0.5 mole)
Al(C$_2$H$_5$)$_2$Cl drop onto 50 g (= 2.18 gram atom) molten
sodium with stirring at 150°C. After cooling, 300 cm^3
dry diethyl ether is added to the reaction mixture with
stirring for about 20 minutes. After the stirring is

stopped, the solid products — NaCl and aluminum — are allowed to settle. The clear ether solution is siphoned off, and the residue is extracted with 200 cm^3 ether. The combined ether solutions, after distilling off the ether and drying in vacuo at 10^{-3} Torr, gives a mixture of $NaAl(CH_3)_4$ and $NaAl(C_2H_5)_4$ in the molar ratio of 1:1. This reaction product melts at 83°C. The yield is practically quantitative.

Example 6

In a manner similar to that described in Example 5, an equimolar mixture of $NaAl(CH_3)_4$ and $NaAl(C_2H_5)_4$ can be prepared by dropping an equimolar mixture of $Al(CH_3)_3$ and $Al(C_2H_5)_3$ (0.67 mole each) onto 23 g (= 1 gram atom) of molten sodium. The reaction mixture is worked up similarly to the way it is described in Example 5.

Example 7

457 g (= 5 moles) $Al(CH_3)_2Cl$ is heated to 80 to 90°C in a dry 1000 cm^3 flask filled with inert gas and fitted with a stirrer and a reflux condenser. 600 g of a 20% suspension of NaH in paraffin oil (containing 120 g NaH = 5 moles) is carefully pipetted onto that solution, and the reaction mixture is stirred for one hour until the solution no longer contains halogen. The reaction mixture, after cooling, is separated from the precipitated NaCl by centrifugation. Using the well known precautions for working with organometallic compounds which are sensitive to air and water, the solution is charged into an autoclave of 2 liters capacity. The contents of the autoclave are heated to 60 to 70°C, with the vessel being shaken or rotated, and ethylene is added to a pressure of 10 to 20 atm. The rapid initial pressure drop makes frequent repressurization with ethylene necessary, until the pressure

/7

10

remains constant after about 45 minutes. Now the excess ethylene is discharged. 600 g of the 20% suspension of NaH (containing 120 g NaH = 0.5 mole) * is added, and the auto-clave is shaken or rolled for 15 to 30 minutes at 80 to 100°C, until all the NaH has dissolved. This can be checked by taking a sample after half an hour. Then ethylene is added to a pressure of 20 atm, and the autoclave is heated to 160°C. The ethylene consumed by the reaction is replaced by repeated repressurizing with ethylene. After 2 to 3 hours there is no more pressure drop, and the reaction is completed.

After the excess ethylene is blown off, the still-liquid contents of the autoclave (i. e., at a temperature above 90°C) are siphoned into a dry two-liter flask filled with inert gas. At 90°C, the reaction product is a two-phase liquid system. The upper layer is paraffin oil, which is practically free of organometallic compounds and is siphoned off from the lower phase. The lower phase is a mixture of $NaAl(CH_3)_4$ and $NaAl(C_2H_5)_4$ in the molar ratio 1:1. It solidifies in crystals at 80°C. The yield of this mixture is 650 g (= 95% of theory).

Example 8

A suspension of 1 kg aluminum granules and as much of a mixture of $Al(C_2H_5)_2Cl$ and $Al(CH_3)_2Cl$ in the molar ratio 1:1 as can be stirred well, about 600 g, are placed in a 10 liter stirring vessel. The reaction vessel is heated to 105 to 115°C. An equimolar mixture of ethyl chloride and methyl chloride in the liquid state (the supply bottle must be upside-down)

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* [Translator's note] Misprint in original text; this should be 5.0 moles, as previously.

is introduced at the bottom of the vessel through a capillary.
Ethyl chloride and methyl chloride in equal amounts can also
be introduced separately through two capillaries.   The
alkyl halides are added at a rate such that the temperature
remains between 105 and 115°C.

Between 350 and 700 g of alkyl chloride are taken up
within an hour.   Within about 6 hours,   3 kg of the mixture
of alkyl halides and all the aluminum used are converted.
In order to convert the resulting mixture of methyl and ethyl
aluminum sesquichloride into $Al(CH_3)_2Cl$ and $Al(C_2H_5)_2Cl$,
or $Al(CH_3)(C_2H_5)Cl$,   425 g of sodium is melted in a second
ten-liter stirring vessel.   The reaction mixture of the
alkyl aluminum sesquichlorides which was obtained is allowed
to drop into the sodium with stirring at 110°C.   After all
has been added,   stirring is continued for another ½ hour.
Finally, the
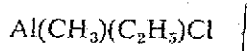
$$Al(CH_3)(C_2H_5)Cl$$

which is formed is distilled off from the sodium chloride
and aluminum at a bath temperature which must be raised to
200°C at the end of the distillation.   One obtains 2.5 kg
$Al(CH_3)(C_2H_5)Cl$,   or 83% of theory.

In order to prepare the complex mixture

$$NaAl(CH_3)_4 - NaAl(C_2H_5)_4$$
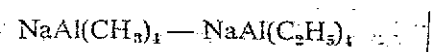
one proceeds similarly to Example 1.   The reaction mixture
just obtained,   with the composition $Al(CH_3)(C_2H_5)Cl$, is allowed
to drop on the corresponding amount of molten sodium.   One
obtains the 1:1 molar mixture

12
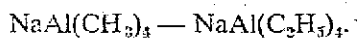
in good yield.

The cathodic deposition of sodium, using the high-conductivity organometallic electrolyte mixture of the invention is described in Examples 9 to 11.

Example 9

One uses a cylindrical steel vessel, enameled on the inside, as the electrolysis cell. The crude sodium to be refined is melted on the bottom. Inside the vessel is hung a cylinder of enameled steel plate, open at both ends, and of somewhat smaller diameter. A coarse net of glass fiber cloth with a mesh of 1 to 3 mm is stretched horizontally over the lower opening of the cylinder. The net is about 3 to 5 mm above the surface of the liquid sodium. Immediately above the net is a net of copper or iron wire as the cathode. The electrolysis temperature is 150°C. As the electrolyte, one uses a mixture of sodium aluminum tetraethyl and tetramethyl in the molar ratio 1:2. The electrolyte melt must rise above the upper edge of the hanging cylinder, so that the cathodic-ally deposited sodium is surrounded above and below by the electrolyte. An electrode current density of 20 A/dm^2 can be maintained with a terminal voltage of 1.1 volts. The sodium formed cathodically collects above the glass fiber net, and can be removed from this space from time to time. By adding crude sodium during the electrolysis one ensures that the distance between the anode and cathode will remain constant.

13

The yield of sodium is 23 g per 26.8 ampere hours.
The same amount of current dissolves 23 g sodium anodically.
The yield is 100%.

Example 10

One proceeds as in Example 9, but replaces the liquid
crude sodium by an equal volume of 1% sodium amalgam. The
electrolysis is done at 150°C with a current density of 30 A/dm^2
at a terminal voltage of 1.7 volts. The sodium deposited
cathodically collects as a confluent liquid layer above the
net of glass fiber cloth. In order to remove the heat from
the current and to mix the electrolyte, one allows a large
supply of electrolyte to flow through the electrolysis cell,
while holding the liquid level in the electrolysis cell constant.
This can be done easily if one allows the same amount of
electrolyte to flow, per unit time, from a supply vessel
into the space between anode and cathode as the volume which
is pumped back again from the point opposite the inlet to the
supply vessel. After 185 ampere-hours, 160 g sodium has
deposited cathodically. The originally 1% sodium amalgam
has been depleted to about 0.2% Na in mercury. It is
conveniently poured out of the cell and, after being
concentrated again to 1% sodium, can be used for a new
electrolysis.

In this test, the same current density (30 A/dm^2) is
attained at about the same voltage (1.5 to 1.7 volts) as
was attained under otherwise equal conditions with an
electrolyte mixture of 80% $KAl(C_2H_5)_4$ and 20% $NaAl(C_2H_5)_4$.

14

Patent Claims

1. Organometallic electrolyte mixture with high conductivity based on sodium-aluminum complex compounds of the general formula $NaAlR_4$ (R = alkyl residue) for the cathodic deposition of sodium, characterized by the fact that it consists of a mixture of $NaAl(CH_3)_4$ and $NaAl(C_2H_5)_4$.

2. Organometallic electrolyte mixture according to Claim 1, characterized by the fact that it consists of 30 to 75 mole percent $NaAl(CH_3)_4$ and 70 to 25 mole percent of $NaAl(C_2H_5)_4$.

3. Organometallic electrolyte mixture according to Claims 1 and 2, characterized by the fact that it contains approximately equivalent amounts of the two components with respect to the tetramethyl complex compound.

4. Organometallic electrolyte mixture according to Claims 1 to 3, characterized by the fact that it also contains small amounts of a corresponding alkoxy complex compound.

5. Organometallic electrolyte mixture according to Claims 1 to 4, characterized by the fact that the sodium aluminum tetramethyl complex compound is prepared by reaction of aluminum trimethyl with sodium, perhaps in the presence of methyl halide, or through reaction with another sodium aluminum tetraalkyl compound, or by reaction of aluminum dimethyl halide and/or aluminum methyl dihalide with sodium.

15

6. Organometallic electrolyte mixture according to Claims 1 to 5, characterized by the fact that one complex component of the mixture is prepared in the presence of the other complex component of the mixture.